

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Group Art Unit: 1791)
Examiner: Monica A. Huson)
Inventor: David B. Naughton)
Serial No: 10/840,022)
Filed: May 5, 2004)
For: METHOD OF MANUFACTURING)
A MOLDED ARTICLE)

**DECLARATION
OF THE
INVENTOR
UNDER
37 C.F.R. §1.131**

Commissioner for Patents
U.S. Patent and Trademark Office
PO Box 1450
Alexandria, VA 22313-1450

Dear Sir:

David B. Naughton hereby declares:

1. That I am the sole inventor of the claimed subject matter of the above identified application.
2. That or before December 3, 2001 I submitted to my academic advisors at the time, Dr. David Nordstrom and Dr. Eric Lokensgard, the thesis proposal attached as Exhibit A, as evidenced by the date of Exhibit A.
3. That I conceived the claimed subject matter claimed in the U.S. patent application entitled "METHOD OF MANUFACTURING A MOLDED ARTICLE" and having Serial No. 10/840,022 in the United States on or before December 3, 2001, as evidenced by the thesis proposal attached as Exhibit A.
4. That I worked diligently towards a reduction to practice of the claimed subject matter from December 3, 2001 until at least May 5, 2004, when the invention

was constructively reduced to practice by filing a patent application with the United States Patent and Trademark Office, as evidenced by: a draft of my thesis paper entitled "SURFACE MODIFICATION OF POLYOLEFIN PLASTICS FORMED BY INJECTION MOLDING" dated August 22, 2002, attached as Exhibit B; a presentation prepared by me in preparation for defense of my thesis in approximately March of 2003, as shown in the electronic mail communication attached as Exhibit C; a draft of the presentation prepared by me in preparation for defense of my thesis in approximately March of 2003, as shown in Exhibit D; a letter from me to Lawrence G. Almeda regarding the filing of a patent application, attached as Exhibit E and dated December 5, 2003; an electronic mail communication from me to Dr. Lokensgard regarding my request to create a prototype dated November 4, 2002 and attached as Exhibit F; and testing data from my laboratory notebook dated January 28, 2003 attached as Exhibit G.

5. That I constructively reduced to practice the claimed subject matter on May 5, 2004 by filing the above identified application with the United States Patent and Trademark Office.

6. That the earliest of the above dates predates the earliest possible priority date of U.S. Patent Application Number 10/887,693, which was filed on July 9, 2004 by Karen S. Rechenberg, which was published as Publication Number 2004/0249075 on December 9, 2004, and which claims priority as a Divisional Application to U.S. Patent Application Number 10/357,817 filed on February 4, 2003, which is a continuation-in-part of U.S. Patent Application Number 10/077,645 filed on February 15, 2002.

7. That the earliest of the above dates also predates the earliest possible priority date of U.S. Patent Application Number 10/058,257, which was filed on January 29, 2002 by Karen S. Rechenberg, which was published as Publication Number 2003/0141620 on July 31, 2003.

8. That all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statement may jeopardize the validity of the above-identified application, and any patent issuing thereon or any patent to which this declaration is directed.

Date: 7/24/08

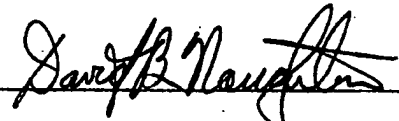

David B. Naughton

Exhibit A

First meeting Dr. Lokensgard/Nordstrom

00-509



CADILLAC PRODUCTS AUTOMOTIVE COMPANY

To: Dr. David Nordstrom and Dr. Eric Lokensgard

From: David Naughton

Date: 12/03/01

Subject: discussion of available resources and timing for my thesis proposal

Purpose: To outline needed resources and determine availability and timing for my thesis proposal.

Present at the meeting were Dr. David Nordstrom, Dr. Eric Lokensgard and myself. The main topics of the meeting were as follows:

1. Questions related to the written proposal
2. Availability of injection molding equipment
3. Forms of priming material available – to include but not limited to chlorinated polyolefins

- Large particle solid (Eastman CPO)
- In solution – 25 % in xylene
- Water base
- Powder form – must be done by a toll manufacturer by conventional or cryogenic grinding

Action required – Dr. Nordstrom to get Eastman contact and e-mail me

4. Discussion of standardized methods (e.g. ASTM) used with the EMU injection molding machine

Action required – Dr. Lokensgard to run molding machine under controlled conditions when samples arrive

5. Polyolefin plastics to be used for evaluation to include, but not limited to polypropylene (Ziegler-Natta, Metallocenes), polyethylene, ethylene/propylene and variations and blends of these plastics

Action required – none, a supply of polyolefin-based plastic is in the lab as per Dr.

Lokensgard

The discussion centered on running a quick test of the proposed bonding process with readily available materials. I am to order a 25 % solution of CPO from Eastman Chemical that I will

spray into a mold of Dr. Lokensgard's choice for drying and injection molding. The results of this test will indicate a direction for future testing. After this testing is complete and shows promise, my interest is in going to a powder form that can be applied in a conventional powder coating process. The source of this powder form will be from conventional or cryogenic grinding and classification. Another method to consider (for academic interest) is super critical carbon dioxide.

Other topics discussed were an explanation of plastic melt flow behavior by Dr. Lokensgard regarding injected plastic contacting a "cold" mold surface and paint adhesion testing of the molded plastic.

D.B.N.

Cadillac Products Automotive Company

Exhibit B

**SURFACE MODIFICATION OF POLYOLEFIN PLASTICS
FORMED BY INJECTION MOLDING**

By

David Brian Naughton

Thesis

Submitted to the Department of Interdisciplinary Technology

Eastern Michigan University

in partial fulfillment of the requirements

for the degree of

MASTERS OF SCIENCE

In

Polymer Technology

August 22, 2002

Ypsilanti, Michigan

APPROVAL

**SURFACE MODIFICATION OF POLYOLEFIN PLASTICS
FORMED BY INJECTION MOLDING**

By

David Brian Naughton

Approved

Dr. J. David Nordstrom

Advisor

date

Dr. Erik Lokensgard

Committee Member

date

Dr. Jamil Bagdashi

Department Head

date

Dr. Robert Holkeboer

Dean of Graduate Studies and Research

date

Dedication

I would like to thank God for the patience of my wife and son, through all the late hours away and distracted conversations. I would also like to thank the many people who chose to be a mentor and guide in the development of this work: Dr. Nordstrom, Dr. Lokensgard and Dr. Baghdachi. Each was a source of support and guidance in their own areas of expertise. I would also like to thank Carl Henderson at EMAL and the University of Michigan for the use of their equipment.

Abstract

Polyolefin plastic (i.e. polypropylene, polyethylene and blends) articles formed by injection molding have been found to have many useful applications. From automotive components to household goods, these plastics are preferred for use when properties of low density, ease of molding, low cost, continued high temperature (104 C) use, chemical resistance and fatigue resistance are needed. Ease of recycling is another of the many reasons these plastics are chosen. The main deficiency of these plastics, beside limited weathering resistance, is the low surface free energy of the molded surface. Many costly and/or hazardous methods are employed to increase the surface energy to a level that promotes the ability of a coating or adhesive to make intimate contact and thereby bond to the molded surface. The proposed method eliminates the need for a carrier medium for the primer and expensive and hazardous surface treatment equipment by modifying the plastic surface during the injection molding process.

This paper is the culmination of approximately three years of work and has included research in plastics, injection molding, powder coating and various instrumentation (e.g. MDSC, SEM, EDS and optical microscopy), physical testing equipment, standardized test methods for plastics and secondary sources covering current research in these areas.

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Bibliography

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Acknowledgements

Chapter 1

Introduction and background

Prior to 1954, propylene polymer - a branched, low molecular weight oil- had a very limited number of uses. After Karl Ziegler and Giulio Natta discovered the use of catalysts to control the manufacture of stereo regular polypropylene, the number of uses for these versatile polymers has increased to the point where global polypropylene production capacity alone was over **10 million tonnes in the 1990s (1990s)**. This rapid growth was fueled by the creation of generation after generation of new catalysts. Each new catalyst type has helped broaden the number of uses and improved the manufacturing of polypropylene and polyolefin plastic. The most recent catalyst - metallocene - not only controls the physical shape of the polymer but it also offers control of the MW and monomer distribution (tacticity) in the production of this polymer. As the understanding of this polymer and the ability to design new variations increases, the market demand for polypropylene continues to grow.

The many advantages of polyolefin plastics, (e.g. they are derived from a relatively inexpensive feedstock, a good balance of physical and mechanical properties and can be

easily recycled) all point to continued growth for this type of plastic. With the advent of new catalysts, control and variation of bulk material properties can be achieved through synthesis. Unfortunately, printability and improved adhesion are only possible by post-polymerization surface modification. This characteristic has significantly limited polypropylene and polyolefin plastic end use applications. Surface modification and the resulting high surface free energy, for the bonding of coatings and adhesives, are the focus of this study.

Objective of this study

In many injection molding applications, polyolefins (i.e. polyethylene, polypropylene and blends) have been preferred for use when the properties of low density, ease of molding, low cost, continued high temperature use (104 C), chemical and fatigue resistance are needed. The main drawback of this type of plastic, beside limited weathering resistance, is the low surface energy (30 dynes/cm) of a molded part. Various methods are employed to increase the surface energy to a level that enables a coating or adhesive to make intimate contact and thereby bond to the surface of the molded article. Methods in use include flame treatment, corona discharge, plasma treatment, chemical solution etching and priming the surface with a halogenated rubber or polyolefin. The priming operation is done either at room temperature or at elevated bake conditions. In an effort to "wet out" the low energy surface, solvents (at ~29 dynes/cm) are preferred to water (at ~ 72.75 dynes/cm) as a carrier medium for the primer, even though water based systems are used in bake applications. So, the conditions under which a halogenated rubber or polyolefin are used are either when dissolved in a low surface tension solvent and air dried or when high heat bake conditions are used to facilitate surface contact (after the water has been removed).

I have worked with many of the surface modification techniques described with varying levels of success. Flame treatment has the obvious hazards and over treatment results in a degraded surface layer. The other treatments listed are limited to only flat surfaces, or are impractical because of high cost. Solvent based solutions of halogenated polymer are flammable and have a high V.O.C. that restricts their use in most manufacturing plants.

My proposal addresses some of the mentioned drawbacks of the above techniques. I propose applying the adhesion promoter (in powder form) in mold when the injection molded part is first made. This eliminates the need for a carrier medium for the polymer and expensive and/or hazardous treatment equipment. The proposed method takes advantage of the heat already supplied by the injection molding process, to attain intimate contact with the cosmetic surface of the plastic molded part.

In order to get the adhesion promoter on the surface of the part, the cosmetic half of the metal mold is utilized. This is done by the electrostatic charging of the classified adhesion promoter (that has polar functional groups on an olefin backbone) in powder form and applying, using standard electrostatic powder coating methods to a grounded mold surface. The electrostatic charge on the powder holds the primer in place (as in a powder coating application) against the grounded mold surface. As the mold is packed and held, the polyolefin portion of the adhesion promoter is free in the melt to associate with and become anchored into the polyolefin plastic injected into the mold, resulting in a part with primer melt applied to the surface of the molded plastic. The two steps of molding the plastic part and priming the surface are combined into one step by this

method. The resulting primed polyolefin plastic surface will be characterized by the high surface energy of the applied primer, allowing for bonding of adhesives or coatings. Each primer type and each grade of plastic has unique processing requirements related to the thermal profile and composition of each material.

Chapter 2

Materials – polyolefin primers

Polyolefin primers come in different composition, Tg, Tm and form i.e. solid, a solution in a high KB solvent or blend and as a particle in a water based dispersion. Many of the solutions are provided at high solids to be later diluted by the customer for use. The choice of primer was based on the thermal profile of the samples, form the sample was available in and known positive effect it had on adhesion. Samples in this study will be identified by A, B,C and D.

	Softening pt.	Chlorine wt %	Acid Number	Form supplied	functionality
Sample A	80-95	18-23	15	powder	Chlorinated, acid
Sample B		26-32		25% in xylene	Chlorinated, acid
Sample C	50	23-25		Powder	Chlorinated, acid
Sample D		0	45-55	25% in xylene	Maleic acid

Chapter 2

Materials – plastics

Current production grades of polyolefin plastics can best be described as copolymers and or blends of polyolefin polymers of either broad or narrow molecular weight distribution with additives. The additives can range from fillers, antistatic aids, nucleating agents, to internal mold release. Due to advances in catalysts used (metallocene), tacticity (and thereby relative % crystallinity) and molecular weight distribution i.e. more narrow distribution, are now controlled by the plastic manufacturer who can tailor properties such as stiffness, impact resistance, clarity and barrier properties into distinct product lines.

My goal in choosing plastic for this study was to find well defined plastic grades that did not have additives in its' composition. I also wanted high and low melt flow rate grades in order to observe the influence flow had on heat transfer. Finally

Chapter 2

Methods – injection molding

Chapter 2

Methods – extrusion mixing

Chapter 2

Methods – primer application

Steps were devised to test the feasibility of this surface modification method. The first step was spraying the primer solution into the metal mold and drying. This was a less likely approach, which had little chance of transfer to the plastic surface. Poor transfer resulted. This was followed by spraying the same primer solution onto a thin Teflon sheet that was dried and placed in mold and the plastic injected into the mold. Transfer of the primer film to the plastic surface was the result of this method. Next, primer in powder form was tried. Initial evaluation was done by first spraying a 33 % solution of polybutene into the mold and drying. This gave a tacky surface that could accept and hold the powder onto the mold surface. The hot plastic enters the mold melting the primer and anchoring it to the parts surface. Surface analysis revealed varying degrees of melt at the

surface of the primed part due to the wide particle size distribution of the solid primer. Particles ranged in size from less than 100 nanometers to over 300 nanometers. This very broad particle size distribution has a high population in the range of ~250-300 micron. Due to the finite amount of heat supplied by the hot plastic when it is injected into the mold, I have observed the large particles do not melt completely (SEM). see image By the definition of T_m , the area under the T_m curve by DSC :

$$T_m = \frac{\text{heat} \times \text{temperature}}{\text{time} \times \text{mass}}$$

From this relationship the amount of material in the mold and the size of the particle is critical to obtaining a good melted surface layer. This situation called for either separating out the large particles or grinding the large particles to within the acceptable range for melting to the plastic surface.

Electrostatic application of the primer in powder form was the goal of this work. Details related to the grounding of the mold, masking of the surface, and application of the powder within the confines of the open mold had to be worked out. The final barrier to evaluating this method was classification of the broad particle size primer powder into a particle size that could be held to the vertical surface of the mold.

Exhibit C

Beaupre, Jon

From: David B Naughton [dnaughton@emich.edu]
Sent: Monday, March 10, 2003 8:40 AM
To: Jamil Baghdachi
Subject: Fwd: Naughton Thesis Defense
Attachments: Naughton Thesis Defense.GWI

Dr. Baghdachi,
Dr. Nordstrom, has indicated I should line up resources to give a 30 minute presentation and thesis defense. I would like to know what I must do to arrange for a room, powerpoint or overhead projector. The date for the defense would be after March 18th.

Thank you,
David Naughton
dnaughton@emich.edu
DNaughton@cadprod.com
248-813-8206

Exhibit D

SURFACE MODIFICATION OF POLYOLEFIN PLASTICS FORMED BY INJECTION MOLDING

SEM Setup

Electron/Specimen Interactions

When the electron beam strikes the sample, both photon and electron signals are emitted.

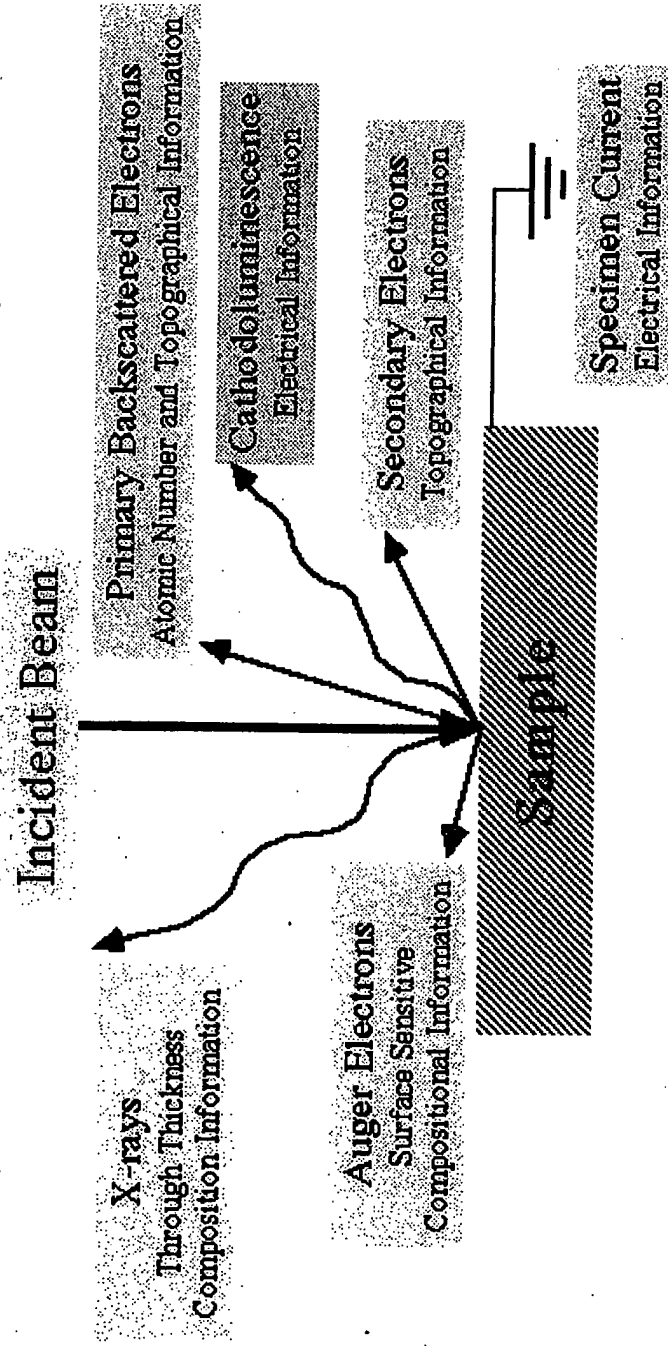


image from http://www.mse.iastate.edu/images/microscopy/spec_interaction.gif

Barriers to using this process

- No control of mold temperature on current equipment
- No idea of the temperature the primer is exposed to (time and temperature) during the molding cycle
- No real measure of the depth of CPO (diffusion) into the PP surface

Abstract

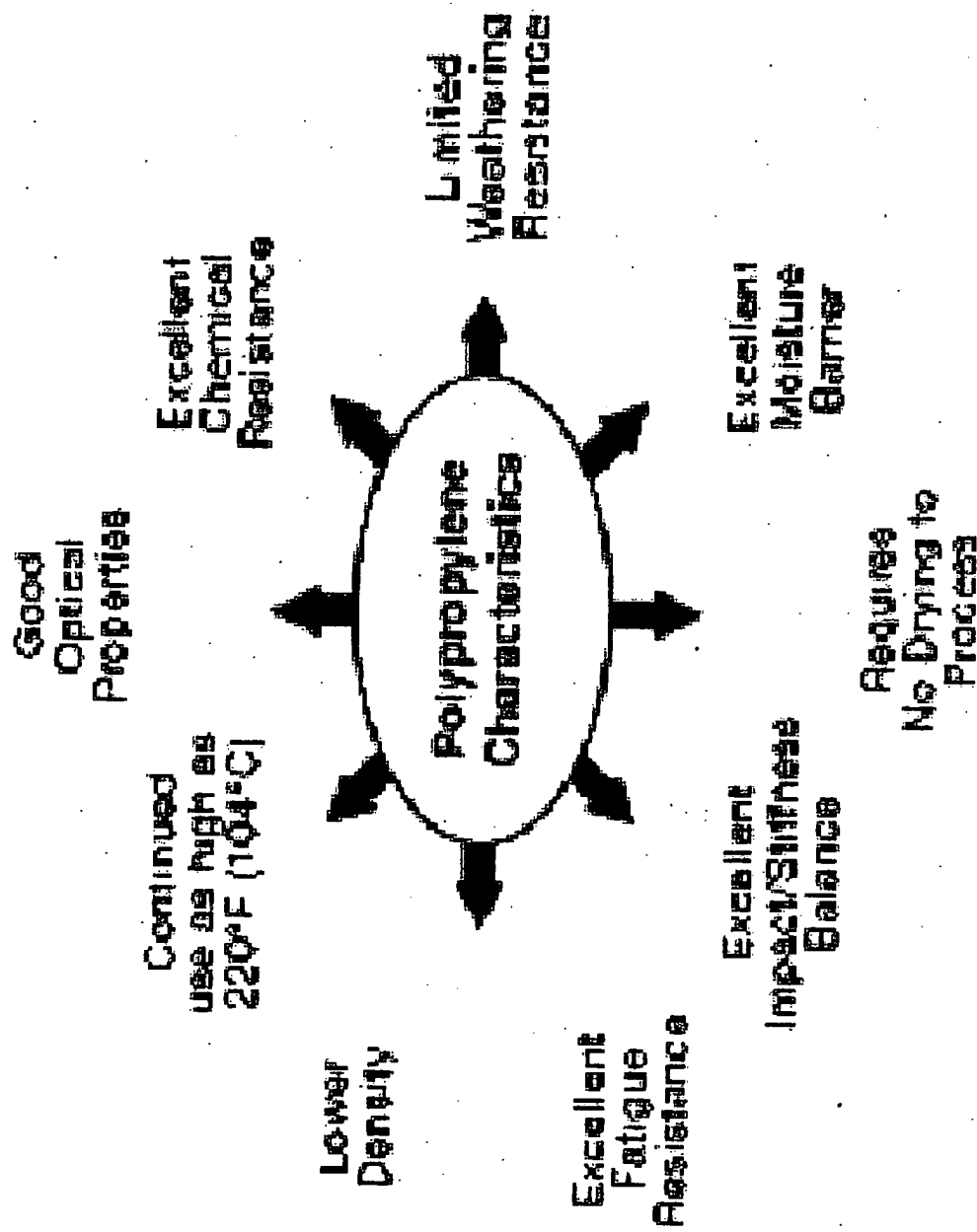
- Polyolefin plastic (i.e. polypropylene, polyethylene, thermoplastic olefin i.e. TPO and blends) articles formed by injection molding have been found to have many useful applications. Many costly and/or hazardous methods are employed to increase the surface energy to a level that promotes the ability of a coating or adhesive to make intimate contact and thereby bond to the molded surface. The method described herein eliminates the need for a post molding process such as solvent or waterborne adhesion promoting primers or expensive, hazardous surface treatment equipment by modifying the plastic surface during the injection molding process.
- The method described in this project was found to be useful in the modification of a nonpolar, polyolefin, plastic surface to that of a polar (determined by energy dispersive spectrometer - EDS) plastic surface, during the injection molding process. This change in polarity of the plastic surface also resulted in improved adhesion of a waterborne paint system.

An interdisciplinary approach was used.

- EMU - Department of Industrial Technology
- The University of Michigan, Electron Microbeam Analysis Laboratory central and north laboratories
- The Coating Research Institute (CRI) for funding.
- Polymer Research Associates (PRA) for use of the MDSC.
- David Pawlik at Energy Conversion Devices, Inc
- Great Western Manufacturing for CPO classification
- Red Spot Paint Company
- Eastman Chemical Company
- Atofina
- ExxonMobil
- Cadillac Products

Background

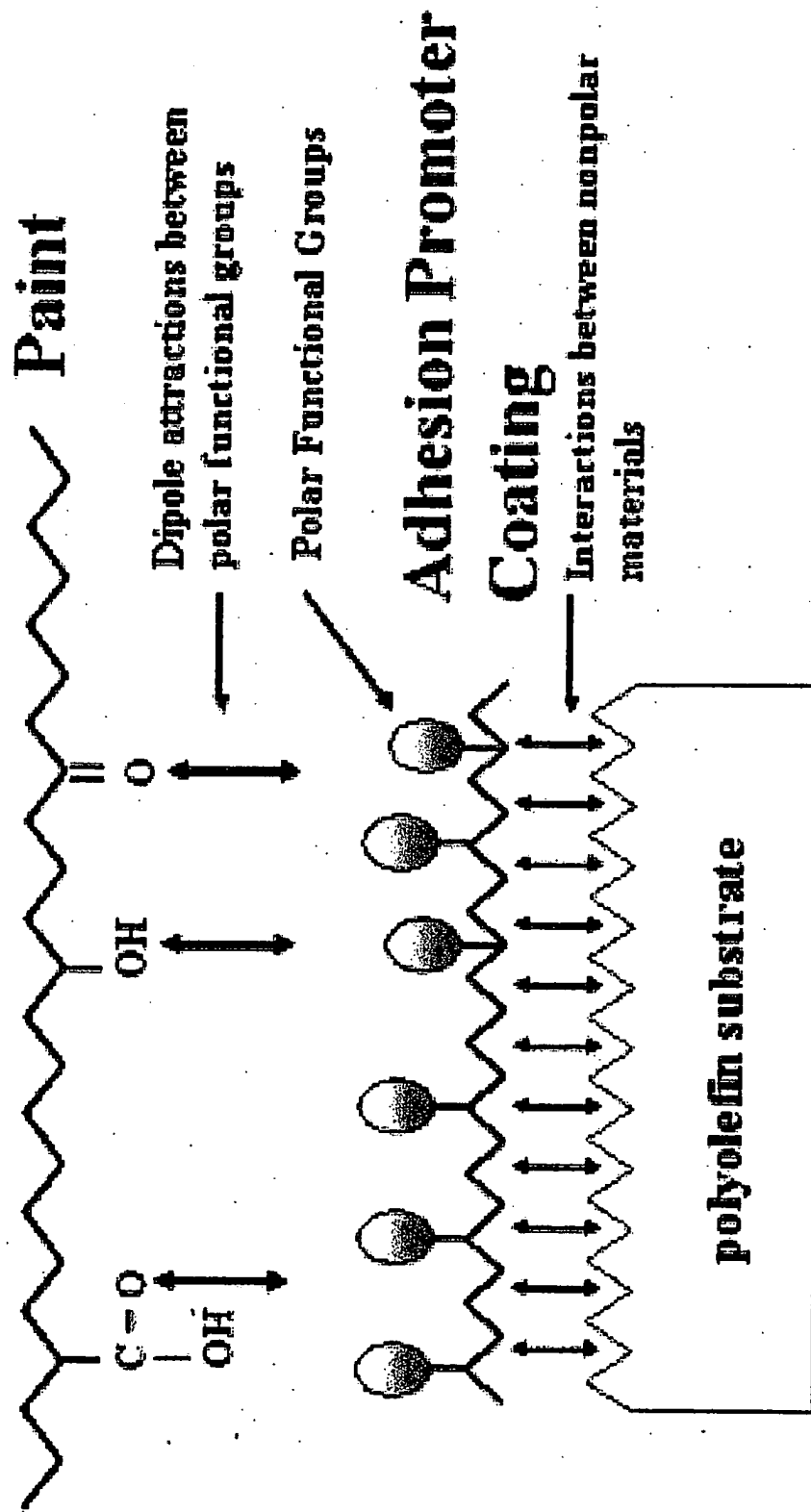
- Polyolefins have many desirable physical properties
- The low surface energy of polyolefins (for the bonding of adhesives or coatings) limit the broad use of this plastic for decorative applications.
- Post-polymerization surface modification is required to improve adhesion and printability.

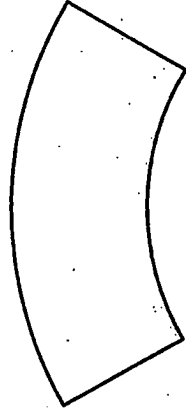


Methods of surface modification to improve adhesion

- Flame treatment
- Corona discharge
- Plasma treatment
- Chemical solution etching
- Priming with a halogenated rubber or polyolefin

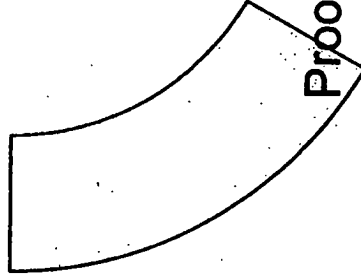
Probable Mechanism for the Function of Adhesion Promoters for
Polyolefins



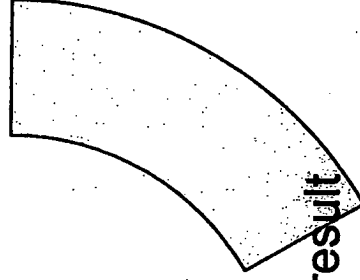


Modify hypothesis

**Feasibility
Try best candidates**

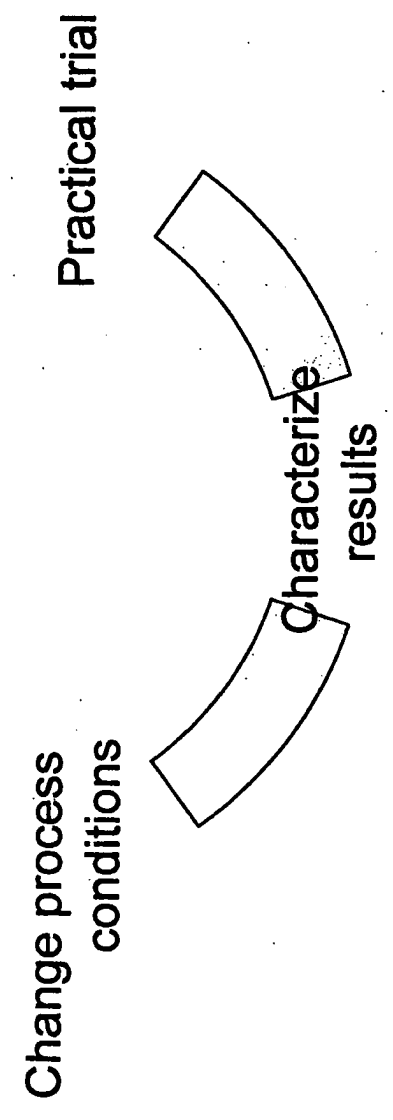
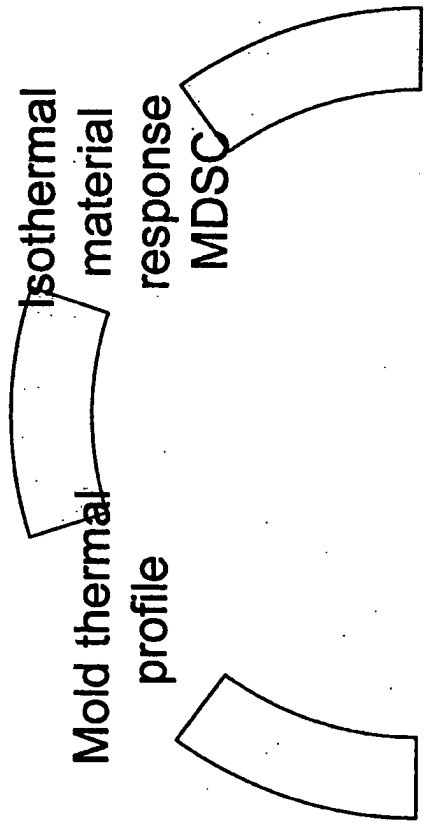


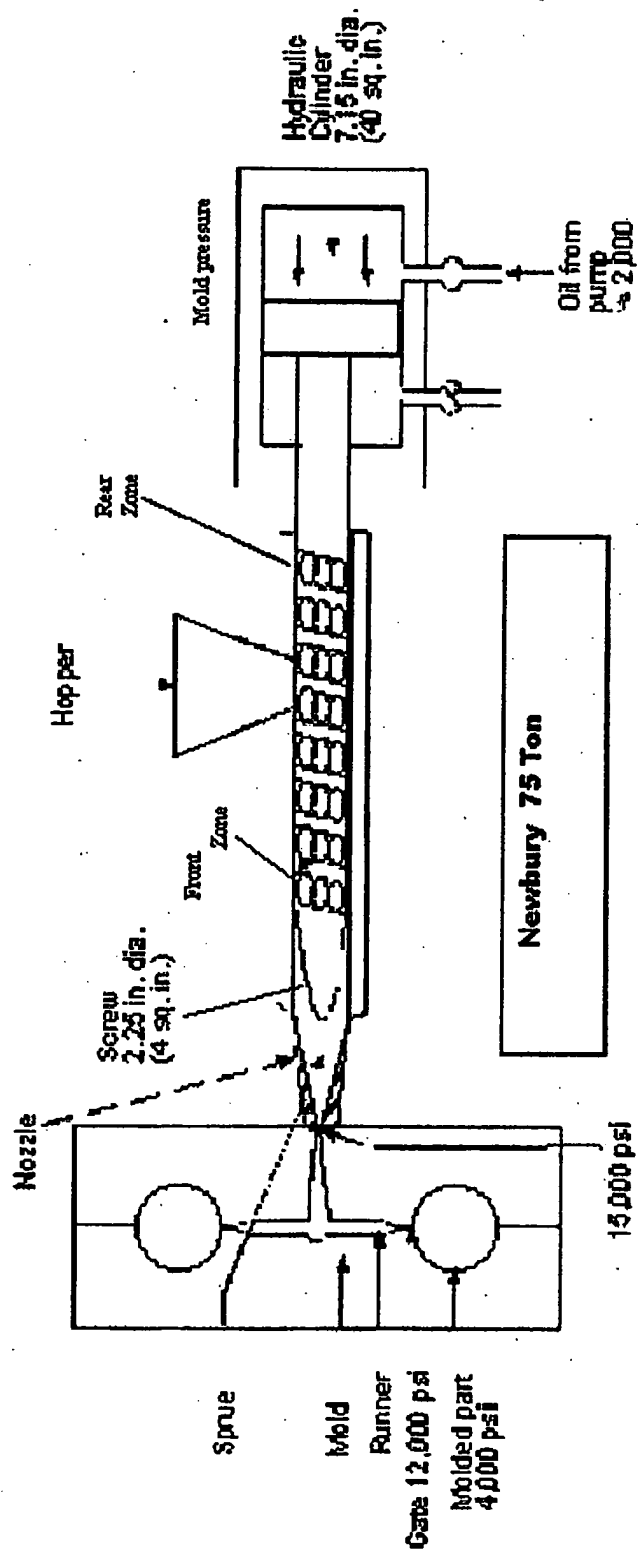
**Proof of desired result
SEM/EDS**

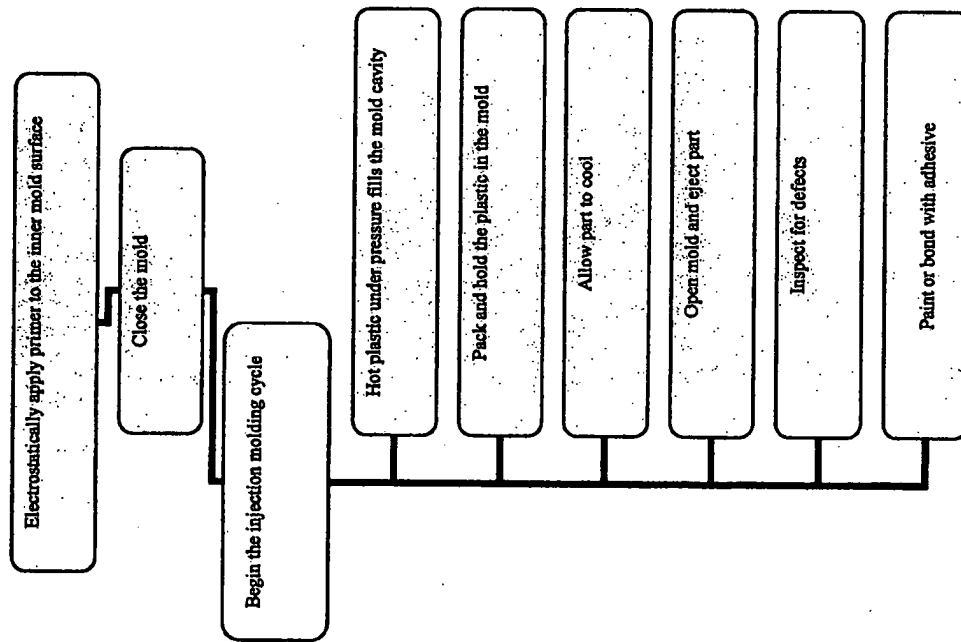


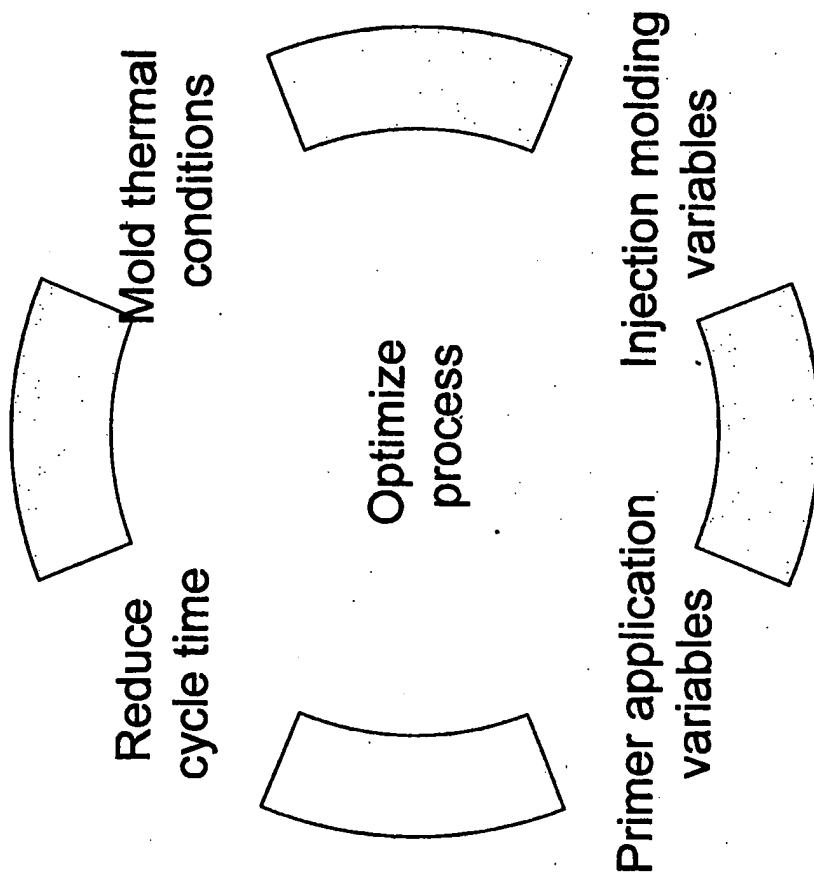
“Ideal” equipment for injection molding evaluation

- Mold temperature control • Equipment not available
- Mold temperature profile at 1/10 of a second interval (Datapaq) • Equipment not available
- Injection molding machine with different mold designs • Equipment was available
- Determine depth of CPO into PP surface • To be determined







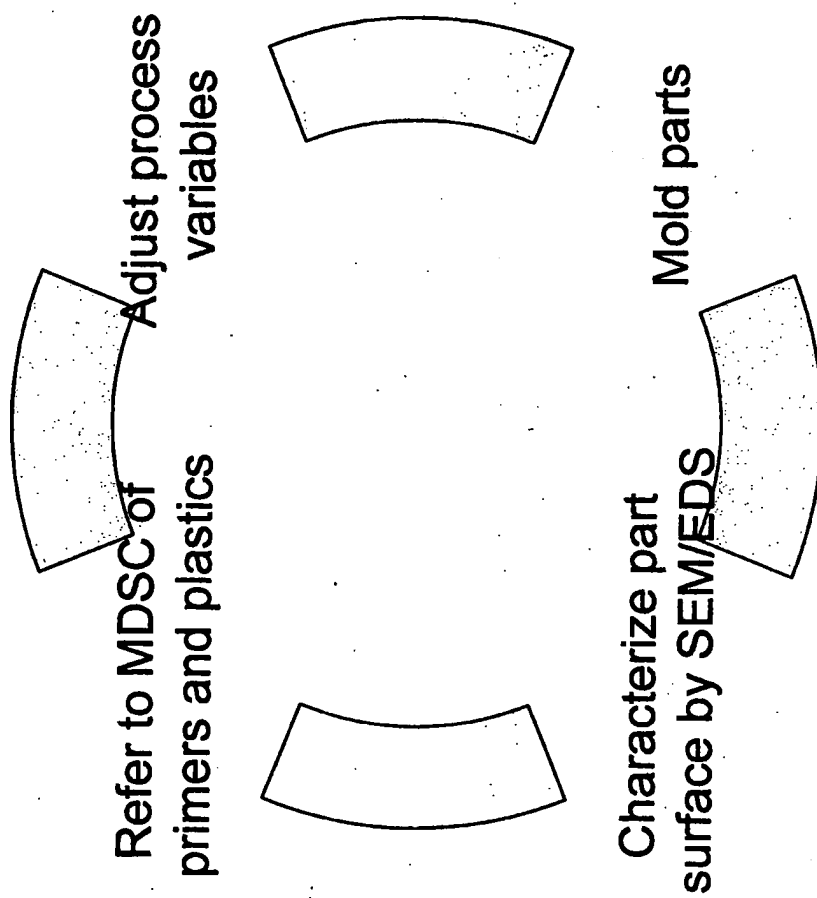


Process variables

- **Mold thermal conditions**
 1. No controls
 2. Constant mold temperature
 3. Increase mold temperature
 4. Chill mold
- **Injection molding**
 1. Molding temperature
 2. Molding pressure
 3. Mold fill rate
 4. Pack time
 5. Hold time

Process variables cont'

- **Primer application**
 - 1. Voltage
 - 2. Powder particle size
 - 3. Powder particle distribution
 - 4. Good ground connection
 - 5. Clean, dry compressed air
- **Reduce cycle time**
 - 1. x/y table for powder spraying
 - 2. MFR of the plastic
 - 3. More crystalline or more amorphous



Verify results

- First use an optical microscope to focus on areas of interest
- Then cut out 20mmx15mm section for carbon coating
- Observe detail at higher magnification
- Determine areas of carbon only by using a control sample – no CPO present by EDS
- Determine areas with CPO by EDS

Feasibility

- Spray apply a CPO solution into the mold, dry and mold the part
- Spray apply a CPO solution onto a Teflon sheet, dry and place in the mold
- spray apply a 33% polybutene solution into the mold for a tacky surface, apply powdered CPO to the tacky mold, remove excess powder

Profile the plastic surface

- Using SEM I could go slowly over the surface taking EDS at points of interest
- Taking multiple EDS readings gave me a profile of the presence or absence of CPO at the plastic surface
- SEM/EDS did not give me a depth of treatment (diffusion into PP surface)

Optical Microscope -vs- TEM -vs- SEM

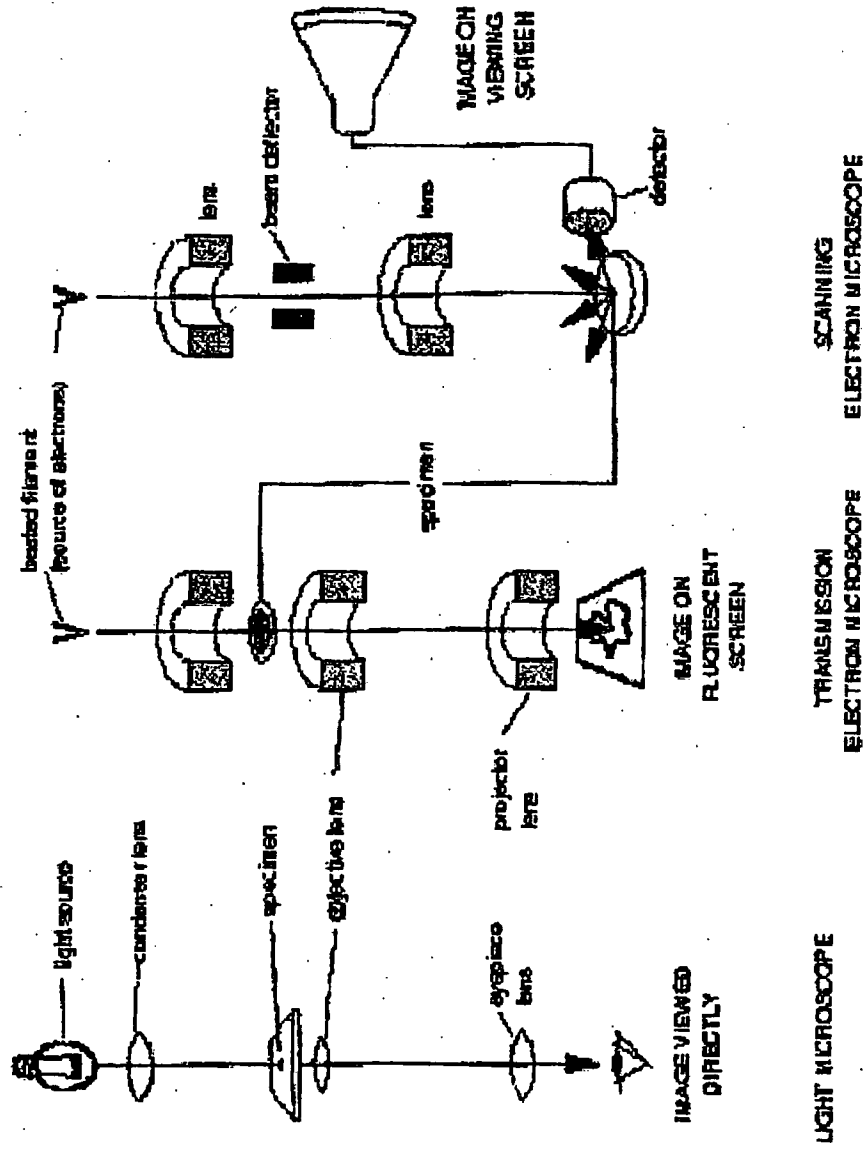


image from: <http://www.mh.uniba.ch/Booklet/Lecture/Chapter1/fig.1-6.gif>

Exhibit E

Friday, Dec. 5, 2003
David B. Naughton

To:
Lawrence G. Almeda
BRINKS HOFER GILSON & LIONE
524 S. Main Street, Suite 200
Ann Arbor, MI 48104
phone: 734-302-6019
fax: 734-994-6331

Solution/invention:

The surface modification methods listed are all secondary operations which normally require large amounts of space for accumulating inventory from the injection molding machine. In some cases a cleaning station is also needed prior to the treatment station, requiring more plant space.

If evaporation or drying is needed permits must be obtained for the removal of V.O.C. The method described in this invention eliminates the need for any secondary operation. Also, no additional heat, ovens or expensive treatment equipment is needed. The source of the heat is as a result of the injection molding process. The heat supplied melts the primer in powder form and penetrates (diffusion) into the plastic surface as the plastic part is formed.

The invention consists of a method of altering the surface character of an injection molded polyolefin plastic article from a non-polar, low surface energy surface to a surface rich (SEM/EDS) in polar halogen functionality. The purpose of this modification is to improve adhesion of various coatings and or adhesives.

Description of the invention:

1. The "cosmetic" side of the mold is grounded (either side or both sides can also be used).
2. A suitable primer, in solid form is classified to within 0-250 micron. *
3. The classified primer is loaded into the hopper of a standard powder coating application equipment and electro-statically charged.

4. The primer, in classified powder form is electro-statically applied to the mold surface (an X, Y, and Z robotic arm may be used to automatically spray the powder).
5. The mold is closed and the injection molding cycle begins.
6. Cooling occurs at the end of the cycle and the modified part is ejected from the mold.
7. A new cycle begins.

* To include but not limited to the CP-343 series of chlorinated/acid functional polyolefin primers from Eastman Chemical Company

Exhibit F

Beaupre, Jon

From: David Brian Naughton [dnaughton@emich.edu]
Sent: Tuesday, July 22, 2008 8:30 PM
To: Beaupre, Jon
Subject: Re: injection molding

Hello DAVE. I can't make parts today at 2:00. I can be available at 3:30 or earlier. If you can be all set-up by then, that will work OK. I may be able to get here sooner, but I'm not sure. I will leave the lab door unlocked, so you can get it. Thanks

- - - - - Original Message - - - - -

From: "David B Naughton" <dnaughton@emich.edu>
Subject: injection molding
Date: 11/04/02 16:58

Dr. Lokensgard,
I would like to make parts with the 4 MFR reactor flake Tuesday at 2:00 11/5/02.

Thank you,

Dave Naughton

Dave Naughton

Exhibit G

Part #	Plaque weight	01-34	Coated w/ ^{nylon arg wt.} RD565 And		
1 primed	41.36 g	980PPK	41.43 g	41.82 g	.39 g
2 primed	41.89 g	529renx	41.97 g	42.39 g	.42 g
3 primed	42.10 g		42.17		
4 primed	41.57 g		41.65		
5 primed	41.50 g		41.57		
6 primed	42.07 g		42.14		
7	41.93 g	980PPK	42.30	.37 g	
8	41.69 g	529renx	42.18	.49 g	
9	41.92 g				
10	41.88 g				
11	41.63 g				
12	41.59 g				
13	42.01 g				
	ave. 41.78 g				

In-mold part

14	42.27 g	980PPK	42.68	.41 g
15	42.18 g	529renx	42.72	.54 g
16		980PPK	42.88	
17		980PPK	43.89	

Continued on Page

Read and Understood By

E. Mangata
Signed

1/28/03
Date

Signed

Date